PATENT SPECIFICATION (11) 1380675

1380675

(21) Application No. 17895/73 (22) Filed 13 April 1973
(31) Convention Application No. 2217746 (32) Filed 13 April 1972 in (19)
(33) Germany (DT)
(44) Complete Specification published 15 Jan. 1975
(51) INT CL² C07F 9/38
(52) Index at acceptance
C2P 1L1 2E11B 2E14 2E18B 2E19B 2E19D 2E20 2E26A 5B 6 7 9
D1P 210 21Y 235 23Y 240 242 24Y 26Y 270 272 274 27Y 36Y 370 385 470 471 47Y 49Y 50Y 510 518 51Y 580 589 59X 59Y 610 62Y 65Y 660 662 66Y L4

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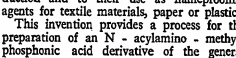
(54) N-ACYLAMINO-METHYL-PHOSPHONATES AND THEIR USE AS FLAME PROOFING AGENTS

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to certain phosphonic acid derivatives, to a process for their production and to their use as flameproofing agents for textile materials, paper or plastics.

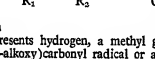
This invention provides a process for the preparation of an N - acylamino - methyl-phosphonic acid derivative of the general formula



(I)

in which

R represents hydrogen, a methyl group, a (C_1—C_4-alkoxy)carbonyl radical or a radical of the formula



R_1 represents hydrogen or a methyl group,

R_2 represents hydrogen, a C_1—C_4-alkyl radical which is optionally substituted by one or more hydroxyl groups and/or halogen atoms, or a C_2—C_4-alkenyl radical, and

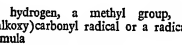
R_3 and R_4 independently of one another represent hydrogen, an alkali metal, alkaline earth metal or ammonium ion, or a C_1—C_4-alkyl radical which is optionally substituted by one or more halogen atoms, or together with the oxygen atoms and the phosphorus atom form a five-membered to seven-membered heterocyclic structure,

in which process an N - acyl - aminomethyl derivative of the general formula

(II)

in which

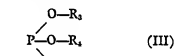
R' is hydrogen, a methyl group, a (C_1—C_4-alkoxy)carbonyl radical or a radical of the formula



R_1 and R_2 have the above-mentioned meanings, and

X represents a dimethylamino or diethylamino group or an acetoxy or propionyloxy radical or, preferably, a halogen atom, especially a chlorine atom, or a hydroxyl group,

is reacted with a phosphorous acid triester of the general formula



(III)

in which

R_3, R_4 and R_5 independently of one another represent a C_1—C_4-alkyl radical which is optionally substituted by one or more halogen atoms, or

R_3 and R_4 together with the oxygen atoms and the phosphorus atom form a five-membered to seven-membered heterocyclic structure,

optionally in the presence of an inert diluent, at temperatures of 40—160°C, preferably 60—130°C. When using N - acylamino-

methyl derivatives of the formula (III) in which X represents an acetoxy or propionyloxy radical, temperatures of 90—150°C have proved advantageous.

The compounds of the formula (I), wherein R_3 and R_4 are hydrogen or alkali metal, alkaline earth metal or ammonium ions, may be prepared by conventional methods that are well-known in the art, for example by hydrolysis of the alkyl esters of the formula (I), optionally followed by neutralization.

The present invention also provides, as new compounds, the N - acylamino - methyl phosphonic acid derivatives of the formula (I), in which R, R_1, R_2, R_3 and R_4 have the meanings stated above, with the proviso that R_3 and R_4 cannot both be unsubstituted alkyl when R, R_1 and R_2 are all hydrogen.

Preferably, R is hydrogen, R_1 and R_2 are each hydrogen or methyl and R_3 and R_4 are each ethyl or chloroethyl.

As examples of representatives of the phosphorous acid triesters of the formula (III) there may be mentioned: trimethylphosphite, triethylphosphite, dimethylethylphosphite, triisopropylphosphite, tri - n - propylphosphite, dimethyl - n - propylphosphite, tri - n - butylphosphite, tri - isobutylphosphite, tris-(chloroethyl) - phosphite, tris - (bromoethyl) - phosphite, 2 - methoxy - 1,3 - dioxa - phospholane and 2 - ethoxy - 4 - methyl - 1,3 - dioxa - phospholane.

As examples of representatives of the N-acyl - amino - methyl compounds of the formula (II) there may be mentioned: N - chloromethyl - N - methyl - acrylic acid amide, N - chloromethyl - N - methyl - methacrylic acid amide, N - (acetoxy - methyl)-methacrylic acid amide, N - (propionyloxy-methyl) - methacrylic acid amide, N - chloromethyl - N - methyl - crotonic acid amide, N - chloromethyl - N - methyl - fumaric acid methyl ester amide, N,N' - bis - chloromethyl - N,N' - dimethyl - fumaric acid diamide, N - bromomethyl - N - methyl-acrylic acid amide, N - (N',N' - diethylamino - methyl) - methacrylic acid amide, N - hydroxymethyl - acrylic acid amide, and N - hydroxymethyl - methacrylic acid amide.

In the reaction, according to the invention, of the compounds of the formula II with the phosphorous acid triesters of the formula III it is advisable continuously to remove the compound R_3X produced in the reaction, for example methyl chloride, ethyl bromide or methyl acetate, from the reaction mixture, for example by distillation or by means of a stream of inert gas. In general, the compounds of the formulae II and III are employed in equimolar amounts, but the phosphorous acid triesters III can also be used in slight excess. (Molar ratios of 1:1 to 1:2).

If appropriate, inert diluents, such as toluene, xylene, n - nonane or dimethylformamide can be used conjointly in the reaction.

It should be pointed out that the reaction of the compounds of the formula II in which X represents an acetoxy or propionyloxy radical, with the phosphorous acid triesters of the formula III represents a new, chemically peculiar reaction.

The compounds of the formula I are capable of numerous uses. Thus, for example, new compounds with valuable properties can be obtained by addition of compounds with active hydrogen atoms to the double bond of the compounds of the formula I. For example, the addition of long-chain amines to the double bond produces surface-active compounds from which compounds having a bactericidal action can be obtained by alkylation or saponification.

The compounds of the formula I can furthermore be polymerised in the usual manner, or be reacted with other polymerisable monomers to give copolymers. The compounds of the formula I are suitable for use as flameproofing agents for textiles of natural or synthetic fibre materials, for example of cotton or regenerated cellulose, polyesters, natural or synthetic polyamides or polyacrylonitrile or their mixtures, and for other materials for example paper and plastics.

Thus, the present invention provides a method of flameproofing a textile, paper or plastics material, which comprises incorporating into the said material a compound according to this invention.

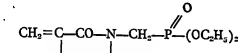
For flameproofing the materials, the present compounds, preferably together with radical donors, such as ammonium persulphate, are applied to the materials, for example from aqueous baths, and subsequently subjected to a heat treatment at 120—200°C or to the action of ionising radiation. Other polymerisable monomers, preferably acrylamide, N - methylol - acrylamide or N - methoxymethyl - acrylamide, can be used conjointly in this treatment.

The parts indicated in the examples which follow are parts by weight, unless stated otherwise.

Example 1

83 parts of triethylphosphite are mixed with 0.5 part of copper powder and heated to 70—80°C. 74 parts of N - chloromethyl-N - methyl - methacrylic acid amide are added dropwise at the same temperature. Ethyl chloride was evolved in an exothermic reaction and is collected in a cold trap cooled with solid carbon dioxide. (Yield: 30 g).

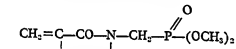
After completion of the addition, the reaction mixture is heated to 70—80°C for a further hour. Thereafter, the almost colourless reaction mixture in the reaction vessel is distilled in vacuo. Yield: 88 g of a colourless liquid of refractive index n_D 1.4634; boiling point: 112—115°C/0.3 mm Hg. The IR spectrum of the product agrees with the structure.



$C_{10}H_{22}NO_4P$ (molecular weight 249)
Calculated:
C: 48.23% H: 8.98% N: 5.62%
P: 12.43%
Found:
C: 47.4% H: 8.4% N: 5.8%
P: 11.9%.

Example 2

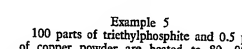
220 parts of trimethylphosphite and 0.5 part of copper powder are reacted, as described in Example 1, with 263 parts of crude N - chloromethyl - N - methyl - methacrylic acid amide at 60—70°C and the mixture is stirred for 1 hour at 70—80°C. The distillation of the reaction mixture yields 230 parts of a colourless liquid of refractive index n_D: 1.4729; boiling point: 108°C/0.1 mm Hg. The IR spectrum of the product agrees with the expected structure.



$C_8H_{16}NO_4P$ (molecular weight 221)
Calculated:
C: 43.44% H: 7.29% N: 6.33%
P: 14.01%
Found:
C: 44.1% H: 7.4% N: 6.7%
P: 13.5%.

Example 3

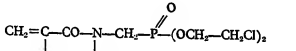
103 parts of trimethylphosphite and 0.5 part of copper powder are reacted, as described in Example 1, with 132 parts of N - chloromethyl - N - allyl - methacrylic acid amide at 80—90°C. The distillation of the reaction mixture yields 82 parts of a liquid of refractive index n_D 1.4805. Boiling point: 117—119°C/0.25 mm Hg. The IR spectrum of the product agrees with the structure.



$C_{12}H_{20}NO_4P$ (molecular weight 247)
Calculated:
C: 48.58% H: 7.34% N: 5.67%
P: 12.53%
Found:
C: 49.1% H: 7.5% N: 5.9%
P: 11.9%.

Example 4

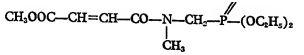
405 parts of tris - (2 - chloroethyl) - phosphite are heated to 100—110°C and 222 parts of N - chloromethyl - N - methylmethacrylamide are added dropwise at the same temperature. At the same time, the dichloroethane formed is distilled off in a stream of nitrogen. After completion of the addition, the pressure is slowly reduced to 0.5 mm Hg, in the course of which the easily volatile constituents distil off. 458 parts of a yellowish viscous liquid, of which the IR spectrum agrees with the structural formula, are left.



$C_{10}H_{15}NO_4PCl_2$ (molecular weight 318)
Calculated:
N: 4.40% P: 9.73% Cl: 22.25%
Found:
N: 4.04% P: 10.45% Cl: 23.40%.

Example 5

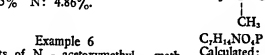
100 parts of triethylphosphite and 0.5 part of copper powder are heated to 80—90°C and 96 parts of N - methyl - N - chloromethyl - fumaric acid methyl ester amide are added dropwise at this temperature. The resulting ethyl chloride is distilled off in a stream of nitrogen. After completion of the evolution of ethyl chloride, the pressure is lowered to 0.5 mm Hg and the temperature raised to 100—110°C and kept at this level until all easily volatile constituents have been distilled off. 138 parts of a reddish-coloured viscous liquid remain, of which the IR spectrum agrees with the structural formula.



$C_{11}H_{22}NO_4P$ (molecular weight 293)
Calculated:
P: 10.57% N: 4.78%
Found:
P: 10.45% N: 4.86%.

Example 6

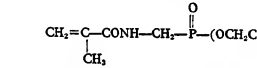
720 parts of N - acetoxymethyl - methacrylic acid amide and 672 parts of trimethylphosphite are mixed at room temperature and 0.5 g of phenothiazine is added. About 200 ml of this mixture are heated in a flask, provided with a column heated to 60°C, a dropping funnel, a stirrer, a thermometer and a gas inlet tube, to 100—110°C until acetic acid methyl ester distils off. Whilst doing this, the apparatus is kept under nitrogen, using the gas inlet tube. The bulk of the mixture is then allowed to run in dropwise over the course of 2—3 hours and finally the mixture is heated to about 125°C until no further acetic acid methyl ester distils off. Excess trimethylphosphite is distilled off at 100°C/10—20 mm Hg. During the subsequent distillation of the residue, 615 g (76% of theory) of a colourless liquid of boiling point 170—180°C/1.2—1.5 mm Hg are obtained. The IR spectrum of the product agrees with the indicated structural formula.



$C_7H_{14}NO_4P$ (molecular weight 207)
Calculated:
C: 40.5% H: 6.5% N: 6.5%
O: 30.6% P: 14.9%
Found:
C: 40.5% H: 7.1% N: 6.4%
O: 30.4% P: 14.7%.

Example 7

71.5 parts of N - acetoxymethyl - methacrylic acid amide and 136 parts of tris - (2 - chloroethyl) - phosphite are mixed at room temperature and 0.2 part of phenothiazine is added. The mixture is introduced dropwise into a flask heated to 120—140°C, in the course of which the resulting acetic acid 2 - chloroethyl ester is distilled off at 20—30 mm Hg through a column heated to 70°C. After completion of the reaction, the volatile constituents are distilled off at 0.5 mm Hg and 130—140°C. 144 parts (95% of theory) of a viscous oil which cannot be distilled are left.

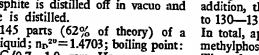


$C_9H_{14}NO_4PCl_2$ (molecular weight 304)
Calculated:
C: 35.4% H: 5.25% N: 4.6%
Cl: 23.3% P: 10.2%
Found:
C: 35.4% H: 5.3% N: 4.3%
Cl: 23.0% P: 10.5%.

Example 8

A mixture, prepared at room temperature, of 164 parts of N - acetoxymethyl - methacrylic acid amide, 210 parts of triethylphosphite and 0.3 part of phenothiazine is allowed to run dropwise into a flask heated to 120—130°C. The acetic acid ethyl ester which forms is distilled off with the aid of a slight stream of nitrogen through a column heated to 80°C. After completion of the reaction, the excess phosphite is distilled off in vacuo and the residue is distilled.

Yield: 145 parts (62% of theory) of a colourless liquid; $n_D^{20}=1.4703$; boiling point: 160—170°C/0.7—1.0 mm Hg.

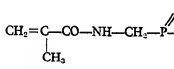


$C_6H_{14}NO_4P$ (molecular weight 235)
Calculated:
C: 46.0% H: 7.65% N: 5.95%
P: 13.2%
Found:
C: 46.3% H: 7.9% N: 6.4%
P: 13.5%.

Example 9

223 parts of trimethylphosphite and 4 parts of hydroquinone are heated to 105—110°C. 174 parts of fused N - hydroxymethyl - methacrylamide are added dropwise at the same temperature from a dropping funnel which can be heated, under a nitrogen atmosphere. At the same time, a mixture of methanol and trimethylphosphite is slowly distilled off through a column. After completion of the addition, the temperature is gradually raised to 130—135°C, until the distillation has ended. In total, approx. 50 parts of a methanol/trimethylphosphite mixture are distilled off. Thereafter the reaction mixture is freed of the easily volatile constituents in a water-pump vacuum at 120°C bath temperature. The lower-boiling constituents are subsequently distilled from the 313 parts of distillation residue in a thin layer distillation apparatus at 0.8 mm Hg and 120°C. Thereafter, 260

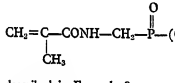
parts of distillation residue are left in the form of a viscous, slightly brownish liquid, which according to analysis by gas chromatography consists to the extent of 78% of the compound of the formula



described in Example 6.

Example 10

146 parts of triethylphosphite and 0.5 part of phenothiazine are heated to 120°C and 135 parts of N - (N',N' - diethylamino-methyl) - methacrylic amid amide are added at the same temperature. The temperature is slowly raised to 160°C, in the course of which 61 parts of an amine mixture of boiling point 69—89°C distil off. Fractional vacuum distillation of the residue yields 71 parts (30% of theory) of a compound boiling at 137—144°C/0.2 mm Hg, which according to examination by gas chromatography is identical with the compound of the formula



described in Example 8.

Example 11

Polyamide carpet material is impregnated with an aqueous liquor which per litre contains 300 g of the compound described in Example 6, 100 g of thiourea, 10 g of cerium nitrate and 1 g of a non-ionic wetting agent. The material is squeezed out to a weight increase of 130% and is dried at 100°C and heated to 120°C for 10 minutes. The flameproof finish thus obtained was tested by the Methenamine Test (DOC FF 2-70), and in particular the carpet material was tested a) after finishing and b) after shampooing three times with a commercially available carpet cleaning shampoo. The material withstood the flameproof test in both cases.

An equivalent flameproof finished was also achieved with a treatment liquor which per litre contained 300 g of the compound described in Example 4, 100 g of thiourea, 50 g of acrylamide, 10 g of ammonium persulphate and 1 g of nonionic wetting agent.

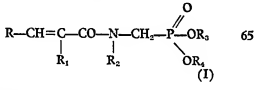
Example 12

Cotton fabric is impregnated on a padder with an aqueous liquor which per litre contains 400 g of the compound described in Example 7, 300 g of acrylamide, 10 g of ammonium persulphate, 4 g of sodium sulphite and 0.5 g of a non-ionic wetting agent, and is squeezed out to a weight increase of 110%. Thereafter the fabric is heated to 100°C for 60 minutes and is then rinsed in warm water and dried.

The flameproofing action of the finish was tested in the vertical test according to DIN 53,906. The fabric withstood the test after finishing even after 5 washing machine washes at 90°C.

WHAT WE CLAIM IS:—

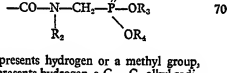
1. N - Acylamino - methyl - phosphonic acid derivatives of the general formula



(I)

in which

R represents hydrogen, a methyl group, a (C_1—C_4-alkoxy)carbonyl radical or a radical of the formula



R_1 represents hydrogen or a methyl group, R_2 represents hydrogen, a C_1—C_4-alkyl radical which is optionally substituted by one or more hydroxyl groups and/or halogen atoms, or a C_2—C_4-alkenyl radical, and

R_3 and R_4 independently of one another represent hydrogen, an alkali metal, alkaline earth metal or ammonium ion, or a C_1—C_4-alkyl radical which is optionally substituted by one or more halogen atoms, or together with the adjacent oxygen atoms and the phosphorus atom form a five-membered to seven-membered heterocyclic structure, with the proviso that R_3 and R_4 cannot both be unsubstituted alkyl when R, R_1 and R_2 are all hydrogen.

2. Compounds according to claim 1, in which R is hydrogen.

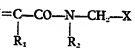
3. Compounds according to claim 1 or 2, in which R_3 and R_4 are identical and represent ethyl or chloroethyl radicals.

4. Compounds according to claim 1, 2 or 3, in which R_1 and R_2 are each hydrogen or a methyl group.

5. Compounds according to claim 1 that are hereinbefore specifically disclosed.

6. A process for the preparation of a compound according to claim 1 (but with the proviso inoperative), in which R is hydrogen, a methyl group or a (C_1—C_4-alkoxy)carbonyl radical, which process comprises reacting an

N - acylamino - methyl compound of the general formula



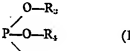
(II)

in which

R′ has the meaning stated above for R, R_1 and R_2 have the meanings stated in claim 1, and

X represents a halogen atom, an hydroxyl, dimethylamino or diethylamino group or an acetoxy or propionyloxy radical,

with a phosphorous acid triester of the general formula



(III)

in which

R_3, R_4 and R_5 each represent, independently of one another, a C_1—C_4-alkyl radical which is optionally substituted by one or more halogen atoms, or

R_3 and R_4 alternatively form, together with the adjacent oxygen atoms and the phosphorous atom, a five-membered to seven-membered heterocyclic structure,

optionally in the presence of an inert diluent, at a temperature of from 40° to 160°C.

7. A process according to claim 6, in which R is hydrogen and R_1 and R_2 are each hydrogen or methyl.

8. A process according to claim 6 or 7, in which X is chlorine or hydroxyl.

9. A process according to claim 6, 7 or 8, in which the reaction is effected at from 60° to 130°C.

10. A process according to claim 6 or 7, in which X is an acetoxy or propionyloxy radical.

11. A process according to claim 10, in which the reaction is effected at from 90° to 150°C.

12. A process according to any of claims 6 to 11, in which R_3, R_4 and R_5 are identical and each represent a methyl, ethyl or chloroethyl group.

13. A process according to any of claims 6 to 12, in which the compound of the formula (II) is one that is hereinbefore mentioned.

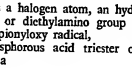
14. A process according to any of claims 6 to 13, in which the compound of the formula (III) is one that is hereinbefore mentioned.

15. A process according to any of claims 6 to 14, in which the compound of the formula (II) and the compound of the formula (III) are employed in a molar ratio of 1:1 to 1:2.

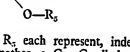
16. A process according to claim 6, substantially as hereinbefore described and/or exemplified.

17. Compounds according to claim 1 whenever prepared by a process according to any of claims 6 to 16.

18. A process for the preparation of a compound according to claim 1, in which R represents a radical of the formula



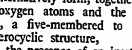
which process comprises reacting a compound of the general formula



(II)

in which

R′ represents a radical of the formula



and

R_1, R_2 and X have the meanings stated in claim 6, with a phosphorous acid triester of the formula (III) as defined in claim 6, optionally in the presence of an inert diluent, at a temperature of from 40° to 160°C.

19. A process for the preparation of a compound according to claim 1, in which R_3 and R_4 represent a hydrogen atom or an alkali metal, alkaline earth metal or ammonium ion, which process comprises hydrolysing a corresponding alkyl ester and, if required, neutralizing the acid so formed.

20. A compound according to claim 1 whenever prepared by a process according to claim 18 or 19.

21. A method of flame-proofing a textile, paper or plastics material which comprises incorporating into the said material a compound according to any of claims 1 to 5 and 17.

22. A method according to claim 21 substantially as hereinbefore described and/or exemplified.

23. A method of flame-proofing a textile, paper or plastics material which comprises incorporating into the said material a compound according to claim 20.

24. A textile, paper or plastics material

whenever flameproofed by a method according to claim 21 or 22.

25. A textile, paper or plastics material whenever flameproofed by a method according to claim 23.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

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